PROCESS FOR MAKING NON-CARCINOGENIC, HIGH AROMATIC PROCESS OIL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention is related to a process for obtaining non-carcinogenic aromatic oils from a mixed distillate and an extract feed obtained in the manufacture of lubricant base oils. A simple feed blending and hydrotreating process is shown for producing aromatic process oil, which shows a mutogenicity index of less than one by a Modified Ames Test.

2. Description of Related Art

In Applicants' recent patent application S/N - 09/455,069, filed on December 6, 1999, a two step approach which is applicable only to a lubricant extract stream is described. The invention described herein covers broader lubricant streams, i.e., blending of a distillate with a lubricant extract stream. It uses a single step approach, and is highly economical relative to our prior method.

Repsol Petroleo patent EP-839891 discloses a process for obtaining aromatic oils with a polycyclic aromatic compounds content of less than 3% (IP-346) from the mixed extract flow obtained in the manufacture of lubricant base oils, a flow which contains a polar solvent, preferably phenol, furfural or N-methyl-2-pyrrolidone (NMP), especially furfural, comprises: (a) cooling the flow of mixed extract to render non-polyaromatic components insoluble; (b) settling to bring about separation of the phases; (c) total or partial redissolution in solvent of the light phase obtained from the settling in (b); (d) cooling to effect separation of the non-polyaromatic

components; and (e) settling to recover the light phase having a low polyaromatic compounds content.

The yield loss by this process is expected to be larger than in the process of the instant invention. Only extraction is used, which removes material from the product. In the instant invention, a blending and hydrogenation steps are used, yield is close to 100% (typically 95-105%).

In EP 0417980A1 patent to BP, process oils with more than 50 weight percent aromatics content (ASTM D 2007) and less than 3% of polycyclic aromatic compounds (IP 346) are obtained by extracting a primary extract (obtained by treatment of a lubricating oil distillate originating from a mineral oil) in a countercurrent extraction column with a polar solvent, using a ratio by volume of primary extract feed: polar solvent of 1:(1-1.8); the top temperature in the extraction column is 50-90 °C, the bottom temperature is 20-60 °C and the top temperature is higher than the bottom temperature. This process of making process oils with a low content of polycyclic aromatic compounds uses a countercurrent extraction process. Extract from the lubes extraction unit is re-extracted by another column (via countercurrent extraction methodology) at low temperatures. The major advantage for this process seems to be that it is a single step process. However, investment costs for a separate countercurrent extractor devoted to a high polycyclic stream is expensive. Using an existing lube extractor for this process might lead to other product contamination with PCA.

WO9844075 patent to Mobil Oil Co. discloses a process for reducing the polycyclic aromatic content of a lubricating oil extract which comprises: (a) extracting vacuum distillates or vacuum residuals with a first extraction solvent to form a primary raffinate and a primary extract mix; and (b) recovering the lubricating oil from the primary extract mix by (c) reextracting the lubricating oil extract with a

second extraction solvent, different from the first solvent, to form a secondary raffinate and secondary extract mix; (d) separating the secondary raffinate from the secondary extract mix; and (e) separating the secondary raffinate and the secondary extract from the second extraction solvent. In this process PCA is removed by re-extracting the lube oil. The second solvent during extraction is different from the first solvent. Applicants' process uses a hydrotreating step as part of the invention.

US patent No. 3,619,414 to Sun Oil is different from Applicants' process. The feed of this process is a "petroleum distillate" and the process is used for improving electrical properties or for obtaining a lighter color. The process describes approximately 30% aromatics in the product.

US patent No. 3,462,358 to Sun Oil Co discloses hydrorefining of the distillates and the product is used for electrical applications. The art of hydrorefining of the distillates is different from hydrotreating.

FR patent 2685705 A1 discloses and claims compositions useful as process oils that are made from mixtures of 'conventionally' processed oils (i.e., distillation, extraction, dewaxing). Hydroprocessing is not mentioned. The resulting process oils are relatively low in aromatics (40-50%).

SUMMARY OF THE INVENTION

An atmospheric distillate stream is combined with a lubricant extract stream. A known quantity, i.e., ratio, of distillate and lubricant extract streams are blended in a mixer/feed tank. This well-mixed stream is then hydrotreated to obtain a product having a desired aromatic content, i.e., non-carcinogenic, high aromatic process oil. This process has more operating flexibility, yield and better efficiency than the processes reported in the prior literature. For example,

desired levels of high aromatic lubricant streams and the desired solvency properties can be achieved by varying the ratio of the feed stream components and hydrotreating conditions.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a schematic drawing of the process according to a preferred embodiment.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

High aromatic content in process oil is desired for many applications. For example, process oil with high aromatic content has been used in ink, pole treating, rubber extenders and in the tire industry. The extracts from lube units typically have high aromatic content (>70%). However, these extracts contain carcinogens. The present invention process removes undesired carcinogens from the feed streams, while maintaining a desired aromatic content, thus making it a desirable product for the above applications.

In the pole treating industry, pole oil is used as a carrier for pentachlorophenol (an insecticide) to treat wood (as a preservative). Development of a non-carcinogenic pole treating oil is a challenging area due to the properties required (a high aromatic, low viscosity stream with a flash point above 150 °F). Using a combination of distillate and extract feed streams and a new process, we have successfully produced pole oil that meets all the specifications of the American Wood Preservative Association (AWPA).

Referring now to Figure 1, a distillate stream, having known properties (such as those shown in Table 1) is fed into a mixer as is well known to those skilled in the art. A lube extract stream, also having known properties (such as those also shown in Table 1) is also fed into the mixer. The two streams are fed in known quantities and in selected ratios,

e.g., those shown in Table 1. The two streams are well-mixed in the tank by mixing/stirring e.g., for one hour at 50 °C. The objective of this step is to have a homogeneous mixture for the hydrotreating step. Thus, mixing time and temperature could be varied to get a homogeneous blend mixture. After the two streams are well mixed, the resulting mixture is fed into a hydrotreater where it is processed under predetermined conditions, as is also well known to those skilled in the art. The resulting process oil exits the hydrotreater having the desired characteristics of high aromaticity and being non-carcinogenic.

Test results for selected feed ratios of selected feeds are tabulated in Table 1. Properties of one of the atmospheric distillates used for making a feed are listed in Table 1. In this method, different cut distillates of a vacuum or atmospheric distillation unit could be used. List of properties of the lubricant extract stream used as a feed component is noted in the next row. In this method, extract from different cuts of distillates of a lube vacuum or atmospheric distillation unit could be used. Also, properties of a feed stream for the hydrotreator are detailed in Table 1 as Feed 1, Feed 2, and Feed 3. These feed streams are prepared by blending the above two components (for example) at various ratios as shown in the Table. Feed 1 was hydrotreated in Run #1 under the specified conditions (Table 1). An appropriate hydrotreating catalyst could be selected (e.g., from the group consisting of Nickel-Molybdenum and Nickel-Cobalt catalysts). As is well-known to those skilled in the art of hydrotreating, a hydrotreating process is performed at a pressure in the range of 400-3000 psi and at a temperature in the range of 400-800 °F. A significant reduction in Sulfur content was achieved by hydrotreating, while keeping almost the same level of aromaticity as shown by comparison of the UV Aromatics data in the table. UV Aromatics is a standard UV spectrophotometric

method wherein an aromatic type in lubricant base oils is measured. Using this method one could measure the amount of benzenes (monoaromatics), naphthalenes (diaromatic), phenanthrenes (triaromatics), chrysenes, tetraphenes, and polyaromatics in mmol/100 gram of oil sample. A slight increase in the aromaticity relative to feed could be due to a change in molecular weight.

The Modified Ames test result shows that the MI of the product obtained in Run #1 is less than 1 indicating it to be non-carcinogen. Similar results were observed in the case of runs using Feed 2 and Feed 3. ASTM D2887 is a simulated distillation method using an automated gas chromatograph. The results are detailed in the examples section below, and gives boiling ranges of the feed and the products.

A lower level of total aromatic content was observed in Runs 2 - 4 than in Run #1 due to the lesser quantity of extract stream in Feed 2 than in Feed 1. This was further illustrated in Runs 5 - 10. Thus, aromatic content may be tailored for desired results by varying the quantity of extract in the feed stream in addition to the standard variations used during the hydrotreating step (e.g., pressure, temperature, catalyst, rate, etc.).

The general procedure followed for feed preparation and for hydrotreating is as follows:

(a) <u>Example 1</u> (Feed 1 in Table 1): Distillate extracts (25 wt. %) and a distillate (75 wt. %) were mixed well by stirring at 50 °C for one hour. The sample was drawn out and its properties were measured: Density 0.9120 g/cc at 60 °F and the other feed properties are listed in Table 1 for Feed 1.

(b) <u>Example 2</u> (Feed 2 in Table 1): Distillate extracts (20 wt. %) and a distillate (80 wt. %) were mixed well by stirring at 50 °C for one hour. The sample was drawn out and its properties were measured: Density 0.9046 g/cc at 60 °F;

D2887E Distillation 5% 411, 50% 509, 95% 939 °F; and the other feed properties are listed in Table 1 for Feed 2.

(c) Example 3 (Feed 3 in Table 1): Distillate extracts (15 wt. %) and a distillate (85 wt. %) were mixed well by stirring at 50 °C for one hour. The sample was drawn out and its properties were measured: Density 0.8989 g/cc at 60 °F and the other feed properties are listed in Table 1 for Feed 3.

(d) Example 4 (Typical hydrotreating procedure, Run # 1, Table 1): The feed (as detailed in Example 1 above) was used. The feed was hydrotreated in a hydrotreating unit using a typical lube oil hydrotreating catalyst (Ni-Mo or Ni-Mo-Co, etc.) at a liquid hourly space velocity (LHSV) of 0.5, at 550 °F and at 1000 psi hydrogen pressure. The unit was allowed to line-out for several hours before collecting the sample. The product has density 0.9215 g/cc at 60 °F; D2887E Distillation 5% 436, 50% 552, 95% 957 °F; Kinematic viscosity 13.31 cSt at 40 °C, 2.8 cSt at 100 °C; Minimum of 10% pentachlorophenol solubility. The other properties of the product are listed in Table 1.

(e) Example 5 (Typical hydrotreating procedure, Run # 2, Table 1): The feed (as detailed in Example 2 above) was used. The feed was hydrotreated in a hydrotreating unit using a typical lube oil hydrotreating catalyst (Ni-Mo or Ni-Mo-Co, etc.) at a liquid hourly space velocity (LHSV) of 0.5, at 550 °F and at 1000 psi hydrogen pressure. The unit was allowed to line-out for several hours before collecting the product. The product has density 0.91 g/cc at 60 °F; D2887E Distillation 5% 443, 50% 542, 95% 942 °F; Kinematic viscosity 10.3 cSt at 40 °C, 2.43 cSt at 100 °C; Minimum of 10% pentachlorophenol solubility; Pour Point -70 °F; Color L4.5; D2549: Saturates 62.84%, Aromatics 36.32%, Polars 0.84%. The other properties of the

Table 1. Test Results

Sample Description	Hydrotreating Conditions: Space Velocity	Hydrotreating Conditions: T °F	Hydrotreating Conditions: H_2 psi	S ppm	N ppm	UV Aromatics, mmol/100g: Total aromatics	UV Aromatics, mmol/100g: Diplus aromatics	UV Aromatics, mmol/100g: Benzenes	UV Aromatics, mmol/100g: Naphthalenes	UV Aromatics, mmol/100g: Phenanthrenes	UV Aromatics, mmol/100g: Chrysenes	UV Aromatics, mmol/100g: Tetraphenes	MI*
Lubricant atmospheric distillate used as a feed component				3230	129	70.40	1.46	68.94	1.09	0.23	0.12	0.02	
Lubricant extract stream used as a feed component				13100	11400	211.50	137.22	74.25	41.66	45.20	33.07	17.29	
Feed 1. (Distillate:Extract: 75:25)				5800	2810	102.60	35.20	67.35	11.73	11.38	8.02	4.07	
Run # 1	0.5	550	1000	2340	3670	129.50	41.39	88.14	16.73	12.72	7.94	4.00	0.77
Feed 2. (Distillate:Extract: 80:20)				5420	2270	109.80	30.72	79.09	10.62	9.70	6.89	3.51	
Run # 2	0.5	550	1000	2040	2890	126.90	35.20	91.74	14.60	10.65	6.65	3.30	0.80
Run # 3	0.5	600	1000	818	2790	121.60	27.16	94.41	10.88	8.21	5.69	2.38	
Run # 4	0.5	550	1000	2080	3110	126.24	36.55	89.69	15.03	10.99	7.01	3.52	
Feed 3. (Distillate:Extract: 85:15)				4550	1610	95.30	22.71	72.58	8.13	7.04	5.02	2.52	
Run # 5	0.5	550	1000	1520	2160	111.50	25.03	86.46	10.44	7.49	4.74	2.36	
Run # 6	1	500	1000	3650	2060	106.57	25.37	81.20	10.37	7.58	4.90	2.52	
Run # 7	1	550	1000	2150	1990	104.30	23.24	81.06	9.67	6.87	4.39	2.31	0.68
Run # 8	1	550	900	2280	1890	104.08	23.57	80.51	9.80	6.95	4.46	2.36	
Run # 9	0.5	550	900	1790	2400	118.09	27.53	90.56	11.59	8.08	5.20	2.66	
Run # 10	1.5	550	1000	3420	1820	98.20	21.29	76.86	8.58	6.43	4.13	2.15	0.67

*MI is Mutogenicity Index measured by Modified Ames Test (MI<1 is considered non-carcinogen).